

MODELING FOR THE DIFFUSION LIMITATION OF FREE RADICAL POLYMERIZATION*

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Abstract: A new model was developed to describe the diffusion limitation on free radical polymerization. In this model the termination rate coefficient (k_t) and propagation rate coefficient (k_p) were expressed as a function of bulk viscosity (η). This model was used to simulate the batch thermal polymerization of styrene (St) and the continuous thermal bulk copolymerization of St (monomer 1) and maleic anhydride (MAH, monomer 2) in a CSTR with on-line monitor of the rheological behavior. The simulated results on polymerization conversion, copolymer composition, molecular weight and its distributions were compared with the experimental data, and the results calculated by two previous gel-effect models i.e. Martin-Hamielec and Tulig-Tirrell models. It was found that the present model produces better prediction than that of the Tulig-Tirrell model and has the same accuracy as that of the Martin-Hamielec model, but is much simpler.

Key words: modeling, diffusion controlled polymerization, bulk viscosity

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INTRODUCTION

It is well known that in free radical polymerization, the diffusion controlled processes strongly influence the rate of polymerization and the properties of the produced polymer. A number of models were developed to describe this phenomena quantitatively (Achilias et al., 1988; Achilias et al., 1992a; Achilias et al., 1992b; Cardenas et al., 1977; Chui et al., 1983; Hui et al., 1972; Ito, 1980; 1981; Marten et al., 1979; Marten et al., 1982; O'Neil et al., 1997; Sharmal et al., 1988; Soh et al., 1982; Tulig et al., 1981; Vivaldoo-Lima et al., 1994), among which the Martin-Hamielec (Marten et al., 1979; Marten et al., 1982) model (MH), Chiu-Carratt-Soong (Chiu et al., 1983; Sharmal et al., 1988) model (CCS), Soh-Sundberg (Soh et al., 1982) model (SS), Achilias-Kiparrissides (Achilias et al., 1988; Achilias et al., 1992a; Achilias et al., 1992b) model (AK), Tulig-Tirrell (Tulig et al., 1981) model (TT) are popular. In all the models, the expressions for termination rate coefficient, k_t and propagation rate coefficient, k_p are composed of a chem-

ical (reaction) term and a physical (diffusion) term. The chemical term depends on the characters of the radicals and monomers, the physical term depends on the physical environment of the reactants. According to the way in which the two terms are coupled together, these models can be divided into two categories: "serial" model and "parallel" model. The MH model, TT model and SS model for k_t are the "serial" models. The CCS model and AK model are the "parallel" models. A significant difference between the "serial" model and "parallel" model is the onset point of diffusion influence on k_t and k_p . In the "parallel" models, allowance is made for the onset of diffusion limitation as the moment polymerization begins. In the "serial" model, the k_t and k_p are considered as constants until their corresponding critical concentrations (C_{crit}) are reached. Turner (Turner, 1977) suggested that the onset of the gel effect is identified with the onset of entanglement in the polymerizing mixture, and the dependence of C_{crit} on the molecular weight (M_w) of the polymer is described by Eq (1)

$$K = C_{crit} M_w^{-\alpha} \quad (1)$$

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Here, the constant $0.5 < \alpha < 1$. In general, the onset of diffusion limitation on k_p is later than that on k_t . It was supposed that this phenomenon only takes place at the below glass transition temperature of the polymerizing mixture. Vivaldoo-Lima et al. (1994) claimed that the physical picture of the "parallel" model may not be correct.

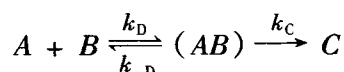
The key task of modeling the diffusion controlled polymerization is how to calculate the diffusion term. Cardens and O'Driscoll (1977) postulated that k_t is inversely proportional to entanglement density. This leads to a function depending on

$$k_t \propto \frac{1}{\phi_p N} \quad (2)$$

Here, ϕ_p is the volume fraction of polymer, N is the chain length. In the most recent studies, the free volume theory and reptation theory are used for the computation of the diffusion coefficients of macromolecule and monomer, and the k_t and k_p are connected with the free volume or polymer concentration. In our recent work, a continuously stirred tank reactor (CSTR) with on-line monitoring of agitation torque was used. The rheological data and kinetics data of the reaction system during the polymerization were obtained. This paper describes a new gel effect model developed to describe the effect of bulk viscosity on k_t and k_p . The model was tested against batch polymerization of Styrene (St) and the continuous bulk copolymerization of St and maleic anhydride (MAH).

DEVELOPMENT OF A NEW MODEL

The bimolecular reaction between two reactants A and B can be described by the following equation, which takes the diffusion steps into consideration:



Here, A and B may be a monomer molecule or a polymeric radical, C can be a new and long radical or a dead macromolecule. k_D , k_{-D} , k_C are approaching rate, separating rate, and chemical kinetics constants respectively.

Assuming the steady state of the concentra-

tion of "AB" is reached, the apparent kinetic constant (k_I) can take the following form:

$$k_I = \frac{k_C k_D}{k_C + k_{-D}} \quad (3)$$

Here, subscript I accounts for propagation or termination.

If the diffusion steps are slower than the chemical reaction step, i. e., $k_C \gg k_{-D}$, the reaction rate is controlled mainly by the approaching step of the two reactants. In this case, the Smoluchowski equation can be used

$$k_I = k_D = 4\pi r_m (D_A + D_B) \quad (4)$$

Here, D_A and D_B are the self-diffusion coefficients of A and B, r_m is the intermolecular separation radius required for reaction.

Free volume is a useful concept for discussing the mobility of the solvent and chain segments in polymer solution. Three typical free volume theories respectively given by Vrentas and Duda (1977; 1993), Bueche (1962), Fujita (1961; 1991) are frequently used in models for diffusion controlled polymerization. Although the diffusion terms are somewhat different from each model according to various free volume theories, they are all made up of a product of two functions. One is dependent on the average chain length and is expressed as a decaying power function, and the other is related to free volume (V_f) as a decaying exponential, i. e.

$$k_I \propto (M_w)^{-A} \exp(-B/V_f) \quad (5)$$

Here, A , B are constants and A is zero for k_p and ranged from 1 to 3 for k_t .

Another approach for describing the dynamic properties of flexible polymer in "good" solvent was developed by de Gennes (1971; 1976). In his view the motion of a given macromolecule is confined within a virtual "tube" defined by the locus of its interaction (or point of entanglement) with adjacent molecules. The molecule is constrained to wriggle snakelike along its own length, by curvilinear propagation of length defects such as kicks or twists along the tube. This type of motion was termed reptation. As a consequence of this idea together with scaling concepts and renormalization group, the relationship among polymer solution concentration (C), chain length (N) and diffusion coefficient (D)

was described as:

$$D \propto N^{-2} C^{-7/4} \quad (6)$$

This relationship accorded with the experimental results of Klein (1978), Hervet et al. (1979) and Callaghan et al. (1980). This theory was used to deduce the following equation.

$$\eta \propto N^3 C^{3.75} \quad (7)$$

where, η is the bulk viscosity.

This expression was confirmed by Ferry et al. (1970).

Combining Eq (6) and Eq (7) yields the following equation.

$$D \propto \eta^{-7/15} N^{-0.6} \quad (8)$$

As a new gel effect model, we have

$$\begin{aligned} k_t &= k_{t,0} & C &\leq C_{\text{crit}} \\ k_t &= k_{t,0} \eta^{-7/15} \left(\frac{M_w}{M_{w,\text{crit}}} \right)^{-0.6} & C &> C_{\text{crit}} \end{aligned} \quad (9)$$

and

$$\begin{aligned} k_p &= k_{p,0} & C &\leq C_{\text{crit}} \\ k_p &= k_{p,0} \eta^\alpha & C &> C_{\text{crit}} \end{aligned} \quad (10)$$

Here, M_w is the weight-average molecular weight of the produced polymer; $M_{w,\text{crit}}$ is a critical molecular weight; α , a parameter to be estimated; C_{crit} , the critical polymer concentration at which the reptative behavior becomes dominant; C'_{crit} , indicates the onset of diffusion limitation on k_p . The model is used to simulate a variety of bulk polymerization systems, including the batch thermal polymerization of St and the continuous random copolymerization of St and MAH with thermal initiation. Conversion, copolymer composition and the molecular weight data available in the literature and our experiments are compared with the predictions of the present model and other gel-effect models.

BATCH THERMAL POLYMERIZATION OF ST

Hui and Hamileic (1972) provided the most extensive experimental data for thermal polymerization of St in the temperature range of 100 ~ 200 °C. In Hui et al.'s work the mechanism and kinetics model of this polymerization were described in detail.

The thermal initiation rate of St, R_I , is given by (Husain et al., 1978):

$$R_I = 2k_I [M_1]^3 \quad (11)$$

where k_I is the initiation rate coefficient which takes the following form:

$$k_I = 2.19 \times 10^5 \exp(-13810/T) \quad (12)$$

The propagation, termination and chain transfer rate constants at zero conversion were taken from the literature (Duerkon et al., 1967):

$$(k_p)_0 = 1.051 \times 10^7 \exp(-3557/T) \quad (13)$$

$$(k_{fm})_0 = 2.31 \times 10^6 \exp(-6577/T) \quad (14)$$

$$(k_t)_0 = 1.255 \times 10^9 \exp(-844/T) \quad (15)$$

In this paper, three models, the MH model, TT model and the present model, are used to treat the diffusion limitations on k_t and k_p .

The MH model is based on free volume theory (Marten et al., 1982), i. e.

$$\begin{aligned} k_t &= (k_t)_0 & V_f &\geq V_{f,\text{cr}} \\ k_t &= (k_t) \left(\frac{M_{w,\text{cr}}}{W_w} \right)^\alpha \exp\left(\frac{A}{V_f} - \frac{A}{V_{f,\text{cr}}} \right) & V_f &\leq V_{f,\text{cr}} \end{aligned} \quad (16)$$

and

$$\begin{aligned} k_p &= (k_p)_0 & V_f &\geq V_{f,\text{cr}} \\ k_p &= (k_p)_0 \exp\left(\frac{B}{V_f} - \frac{B}{V_{f,\text{cr}}} \right)^{1.75} & V_f &\leq V_{f,\text{cr}} \end{aligned} \quad (17)$$

Where $V_{f,\text{cr}}$ and $V_{f,\text{crp}}$ are critical free volumes for k_t and k_p . The model parameters can be found in the literature (Marten et al., 1982).

In the TT model, which is based on reptation theory, k_p is taken to be a constant and k_t has the forms (Tulig et al., 1981):

$$\begin{aligned} k_t &= (k_t)_0 - \gamma C & C &\leq C_{\text{crit}} \\ k_t &= k_t \left(C_{\text{crit}} M_w^{-2} - \left(\frac{C_{\text{crit}}}{C} \right)^{1.75} \right) & C &> C_{\text{crit}} \end{aligned} \quad (18)$$

Here, the parameters γ and C_{crit} are estimated from the experimental data.

To apply the model developed in this paper, the bulk viscosity of the PS-St solution should be available. Here, the following correlation (Mendelson, 1979) was used:

$$\begin{aligned} \eta(T_R) &= 3.31 \times 10^{-12} C^{10.7} M_w^{3.4} \\ &\exp\left[\frac{2300 \exp(2.4C)}{R} \left(\frac{1}{T_R} - \frac{1}{473} \right) \right] \end{aligned} \quad (19)$$

where T_R is the reaction temperature.

For the present model, it is supposed that the termination is controlled by the diffusion of chain radicals right from the start of polymerization. Therefore, the onset of diffusion limitation on k_p and α in Eq (10) can be estimated from the experimental data. It is very interesting that the ratio of the two exponents in Eqs (9) and (10) is close to the ratio of the two overlapped factors (A and B) in Eqs (16) and (17).

The predictions of these models are compared with the experimental data of Hui et al in figures 1 and 2. It was found that although all the three models can give good predictions for the time evolution of conversion, only the MH model and the present model can simulate well the molecular weight of the produced polymer. The TT model's ignoring the diffusion limitation on k_p causes prediction of higher molecular weight at high conversion.

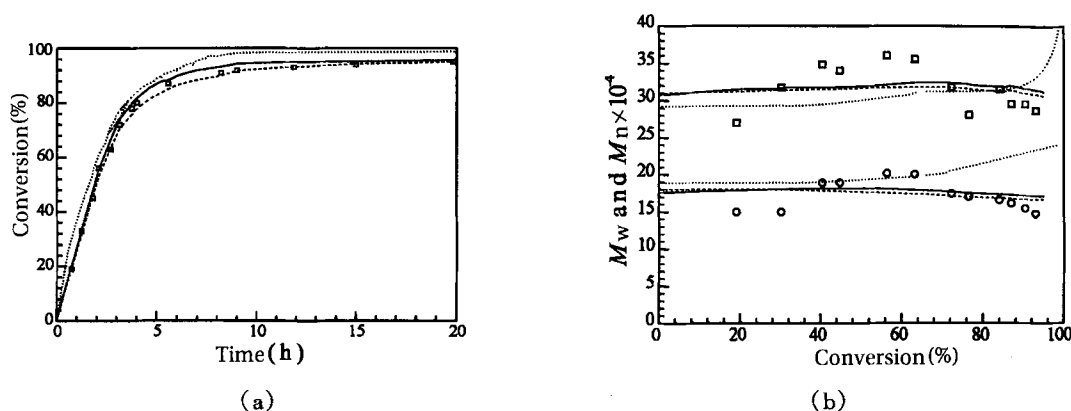


Fig. 1 Conversion(a), weight average and number average molecular weights(b) for batch thermal polymerization of St at 140 °C (experimental data: \square conversion and weight average molecular weight, \circ number average molecular weight; simulated result: —MH model, - - present model, \cdots TT model)

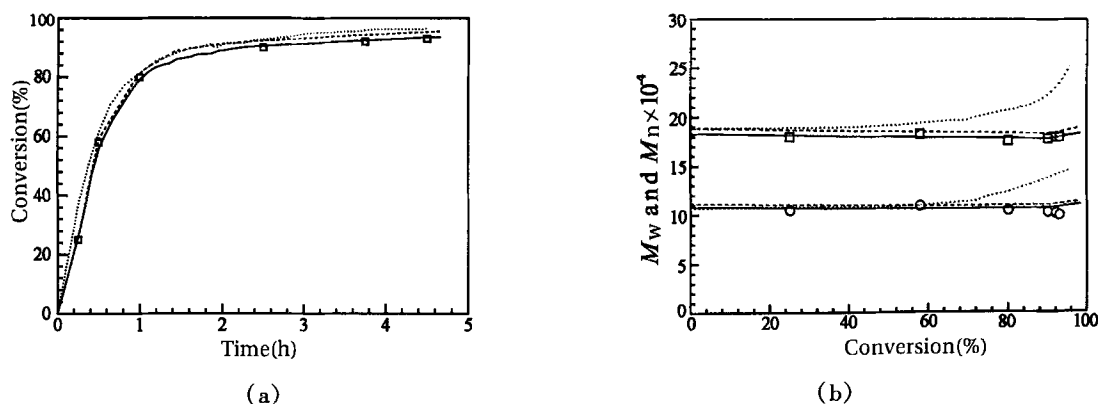
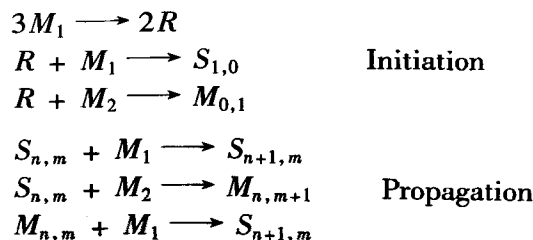
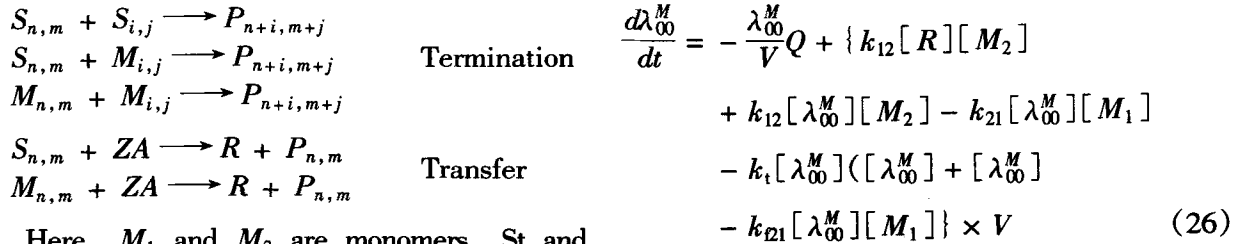


Fig. 2 Conversion(a), weight average and number average molecular weights(b) for batch thermal polymerization of St at 170 °C (Points and curves as described in Fig. 1.)

CONTINUOUS THERMAL COPOLYMERIZATION OF ST AND MAH

The mechanism of the copolymerization of St and MAH is as follows (Yao et al., 1998; 1999):





Here, M_1 and M_2 are monomers, St and MAH; R , the free radical species generated by thermal initiation of St; $S_{n,m}$ ($M_{n,m}$) is the growing free radical species with n unit of St and m unit of MAH with terminal St (MAH); $P_{n,m}$, the dead polymer with n unit of St and m unit of MAH; ZA is the active Dies-Alder adducts of St thermal initiation. It should be noted that only combination termination is taken into account for this mechanism. Otherwise, the MAH homopolymerization is ignored because the maleic free radical on the end of a growing chain can not easily react with MAH monomer (Jones et al., 1969).

Since the reaction was carried out in a CSTR, the following equations summarize the material and energy balances of the reactor with the assumption of perfect mixing

$$\begin{aligned}
\frac{dN_1}{dt} = F_1 - \frac{N_1}{V}Q - (k_{11}[\lambda_{00}^S][M_1] \\
+ k_{21}[\lambda_{00}^M][M_1])V \quad (20)
\end{aligned}$$

$$\frac{dN_2}{dt} = F_2 - \frac{N_2}{V}Q - k_{12}[\lambda_{00}^S][M_2]V \quad (21)$$

$$\begin{aligned}
\frac{dP_1}{dt} = -\frac{P_1}{V}Q + (k_{11}[\lambda_{00}^S][M_1] \\
+ k_{21}[\lambda_{00}^M][M_1])V \quad (22)
\end{aligned}$$

$$\frac{dP_2}{dt} = -\frac{P_2}{V}Q + k_{12}[\lambda_{00}^S][M_2]V \quad (23)$$

$$\begin{aligned}
\frac{dR}{dt} = -\frac{R}{V}Q + (R_I - k_{11}[R][M_1] \\
- k_{12}[R][M_2] + k_{f11}[\lambda_{00}^S][M_1] \\
+ k_{f12}[\lambda_{00}^M][M_1]) \times V \quad (24)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{00}^S}{dt} = -\frac{\lambda_{00}^S}{V}Q + \{k_{11}[R][M_1] \\
+ k_{21}[\lambda_{00}^M][M_1] - k_{12}[\lambda_{00}^S][M_2] \\
- k_t[\lambda_{00}^S](\lambda_{00}^S + \lambda_{00}^M) \\
- k_{f11}[\lambda_{00}^S][M_1]\} \times V \quad (25)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{00}^M}{dt} = -\frac{\lambda_{00}^M}{V}Q + \{k_{12}[R][M_2] \\
+ k_{12}[\lambda_{00}^M][M_2] - k_{21}[\lambda_{00}^M][M_1] \\
- k_t[\lambda_{00}^M](\lambda_{00}^M + \lambda_{00}^S) \\
- k_{f21}[\lambda_{00}^M][M_1]\} \times V \quad (26)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{10}^S}{dt} = -\frac{\lambda_{10}^S}{V}Q + \{k_{11}[R][M_1] \\
+ k_{21}[\lambda_{10}^M][M_1] + k_{11}[\lambda_{00}^S][M_1] \\
+ k_{21}[\lambda_{00}^M][M_1] - k_{12}[\lambda_{10}^S][M_2] \\
- k_t[\lambda_{10}^S](\lambda_{10}^S + \lambda_{10}^M) \\
- k_{f11}[\lambda_{10}^S][M_1]\} \times V \quad (27)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{10}^M}{dt} = -\frac{\lambda_{10}^M}{V}Q + \{k_{12}[R][M_2] \\
- k_{21}[\lambda_{10}^M][M_1] - k_t[\lambda_{10}^M](\lambda_{10}^M + \lambda_{10}^S) \\
- k_{f21}[\lambda_{10}^M][M_1]\} \times V \quad (28)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{01}^S}{dt} = -\frac{\lambda_{01}^S}{V}Q + \{k_{21}[\lambda_{01}^M][M_1] \\
- k_{12}[\lambda_{01}^S][M_2] - k_t[\lambda_{01}^S](\lambda_{01}^S + \lambda_{01}^M) \\
+ k_{f11}[\lambda_{01}^S][M_1]\} \times V \quad (29)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{01}^M}{dt} = -\frac{\lambda_{01}^M}{V}Q + \{k_{12}[R][M_2] \\
+ k_{12}[\lambda_{01}^S][M_2] + k_{12}[\lambda_{00}^S][M_2] \\
- k_{21}[\lambda_{01}^M][M_1] - k_t[\lambda_{01}^M](\lambda_{01}^M + \lambda_{01}^S) \\
+ k_{f21}[\lambda_{01}^M][M_1]\} \times V \quad (30)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{20}^S}{dt} = -\frac{\lambda_{20}^S}{V}Q + \{k_{11}[R][M_1] \\
+ k_{21}[\lambda_{20}^M][M_1] + 2k_{11}[\lambda_{10}^S][M_1] \\
+ 2k_{21}[\lambda_{10}^M][M_1] + k_{11}[\lambda_{00}^S][M_1] \\
+ k_{21}[\lambda_{00}^M][M_1] - k_{12}[\lambda_{20}^S][M_2] \\
- k_t[\lambda_{20}^S](\lambda_{20}^S + \lambda_{20}^M) \\
- k_{f11}[\lambda_{20}^S][M_1]\} \times V \quad (31)
\end{aligned}$$

$$\begin{aligned}
\frac{d\lambda_{20}^M}{dt} = -\frac{\lambda_{20}^M}{V}Q + \{k_{12}[R][M_2] \\
- k_{21}[\lambda_{20}^M][M_1] - k_t[\lambda_{20}^M](\lambda_{20}^M + \lambda_{20}^S) \\
- k_{f21}[\lambda_{20}^M][M_1]\} \times V
\end{aligned}$$

$$+ [\lambda_{20}^M]) - k_{21} [\lambda_{20}^M] [M_1] \} \times V \quad (32)$$

$$\begin{aligned} \frac{d\lambda_{02}^S}{dt} = & -\frac{\lambda_{02}^S}{V} Q + \{ k_{21} [\lambda_{02}^M] [M_1] \\ & - k_{12} [\lambda_{02}^S] [M_2] - k_t [\lambda_{02}^S] ([\lambda_{02}^S] \\ & + [\lambda_{02}^M]) - k_{f11} [\lambda_{02}^S] [M_1] \} \times V \quad (33) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{02}^M}{dt} = & -\frac{\lambda_{02}^M}{V} Q + \{ k_{12} [R] [M_2] \\ & + k_{12} [\lambda_{02}^S] [M_2] + 2k_{12} [\lambda_{00}^S] [M_2] \\ & + k_{12} [\lambda_{00}^S] [M_2] - k_{21} [\lambda_{02}^M] [M_1] \\ & - k_t [\lambda_{02}^M] ([\lambda_{02}^S] + [\lambda_{02}^M]) \\ & - k_{21} [\lambda_{02}^M] [M_1] \} \times V \quad (34) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{11}^S}{dt} = & -\frac{\lambda_{11}^S}{V} Q + \{ k_{21} [\lambda_{11}^M] [M_1] \\ & + k_{11} [\lambda_{01}^S] [M_1] + k_{21} [\lambda_{01}^M] [M_1] \\ & - k_{12} [\lambda_{11}^S] [M_2] - k_t [\lambda_{11}^S] ([\lambda_{11}^S] \\ & + [\lambda_{11}^M]) - k_{f11} [\lambda_{11}^S] [M_1] \} \times V \quad (35) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{11}^M}{dt} = & -\frac{\lambda_{11}^M}{V} Q + \{ k_{12} [\lambda_{11}^S] [M_2] \\ & + k_{12} [\lambda_{10}^S] [M_2] - k_{21} [\lambda_{11}^M] [M_1] \\ & - k_t [\lambda_{11}^M] ([\lambda_{11}^S] + [\lambda_{11}^M]) \\ & - k_{21} [\lambda_{11}^M] [M_1] \} \times V \quad (36) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{00}^P}{dt} = & -\frac{\lambda_{00}^P}{V} Q + \{ \frac{k_t}{2} ([\lambda_{00}^S] + [\lambda_{00}^M])^2 \\ & + (k_{f11} [\lambda_{00}^S] + k_{21} [\lambda_{00}^M]) [M_1] \} \times V \quad (37) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{10}^P}{dt} = & -\frac{\lambda_{10}^P}{V} Q + \{ k_t ([\lambda_{10}^S] + [\lambda_{10}^M]) ([\lambda_{00}^S] \\ & + [\lambda_{00}^M]) + (k_{f11} [\lambda_{10}^S] + k_{21} [\lambda_{10}^M]) \cdot \\ & [M_1] \} \times V \quad (38) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{01}^P}{dt} = & -\frac{\lambda_{01}^P}{V} Q + \{ k_t ([\lambda_{01}^S] + [\lambda_{01}^M]) ([\lambda_{00}^S] \\ & + [\lambda_{00}^M]) + (k_{f11} [\lambda_{01}^S] + k_{21} [\lambda_{01}^M]) \cdot \\ & [M_1] \} \times V \quad (39) \end{aligned}$$

$$\frac{d\lambda_{20}^P}{dt} = -\frac{\lambda_{20}^P}{V} Q + k_t \{ ([\lambda_{20}^S] + [\lambda_{20}^M]) ([\lambda_{00}^S]$$

$$+ [\lambda_{00}^M]) + ([\lambda_{10}^S] + [\lambda_{10}^M])^2 \\ + (k_{f11} [\lambda_{20}^S] + k_{21} [\lambda_{20}^M]) [M_1] \} \times V \quad (40)$$

$$\begin{aligned} \frac{d\lambda_{02}^P}{dt} = & -\frac{\lambda_{02}^P}{V} Q + k_t \{ ([\lambda_{02}^S] + [\lambda_{02}^M]) ([\lambda_{00}^S] \\ & + [\lambda_{00}^M]) + ([\lambda_{01}^S] + [\lambda_{01}^M])^2 \\ & + (k_{f11} [\lambda_{02}^S] + k_{21} [\lambda_{02}^M]) [M_1] \} \times V \quad (41) \end{aligned}$$

$$\begin{aligned} \frac{d\lambda_{11}^P}{dt} = & -\frac{\lambda_{11}^P}{V} + k_t \{ ([\lambda_{11}^S] + [\lambda_{11}^M]) ([\lambda_{00}^S] \\ & + [\lambda_{00}^M]) + ([\lambda_{10}^S] + [\lambda_{10}^M]) ([\lambda_{01}^S] \\ & + [\lambda_{01}^M]) + (k_{f11} [\lambda_{11}^S] + k_{21} [\lambda_{11}^M]) \\ & [M_1] \} \times V \quad (42) \end{aligned}$$

Here, the ij -th moments are defined as

$$\lambda_{ij}^S = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^i m^j S_{n,m}$$

$$\lambda_{ij}^M = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^i m^j M_{n,m}$$

$$\lambda_{ij}^P = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} n^i m^j P_{n,m}$$

$[M_1]$ and $[M_2]$ are molar concentrations of St and MAH; Q volumetric flow out of the reactor; V available volume of reactor; k_t is the termination rate coefficient; k_{ij} , the coefficients for various propagation reactions; $k_{f,ij}$, the rate constants for chain transfer; $[A]$, the molar concentration of species A.

In this work, the continuous thermal bulk copolymerization of St/MAH was conducted under different operating conditions. The agitator torque was measured on-line and converted to the bulk viscosity of the polymerizing medium. In figures 3 ~ 5, the predictions from the three gel-effect models (MH, TT, and present models) are compared with experimental results on the time evolution of conversion (C%), the MAH weight fraction in copolymer (MAH%), the weight-average molecular weight (M_w) and the molecular weight polydispersity.

It can be found that the deviation of the predicted profiles of the T-T model from experimental results is quite large in the region of relatively high conversion. The discrepancies are also due to the ignoring of the diffusion limitation on k_p .

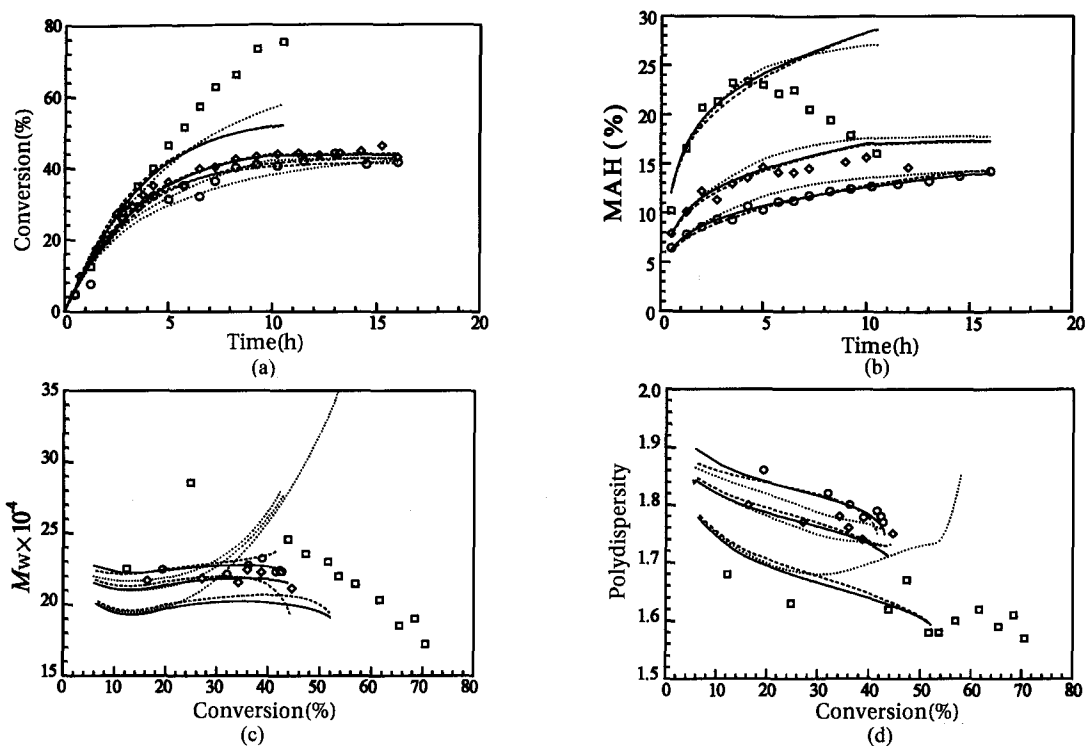


Fig. 3 Conversion(a), copolymer composition(b), molecular weight(c) and its distribution(d) for continuous copolymerization of St and MAH with different MAH weight fractions in inflow (experimental data for MAH weight fraction in inflow = \circ 7w%, \diamond 10w%, \square 20w%; $T = 110\text{ }^{\circ}\text{C}$, $\tau = 5\text{ h}$; curves as described in Fig. 1)

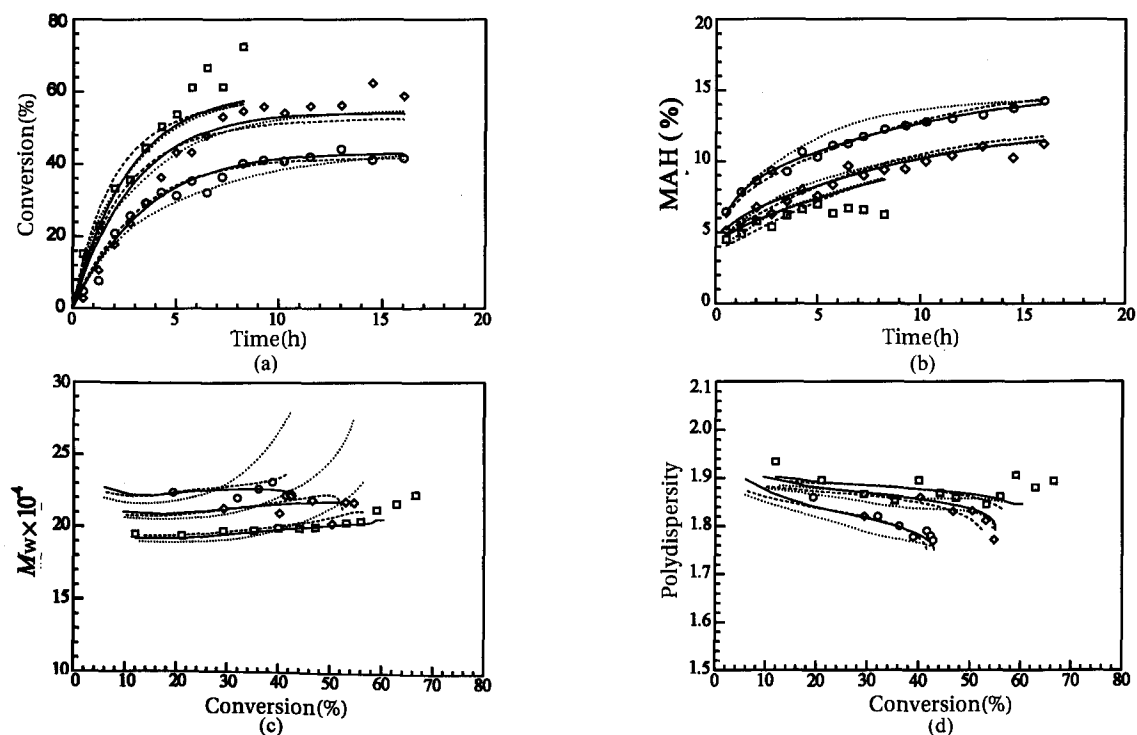


Fig. 4 Conversion(a), copolymer composition(b), molecular weight(c) and its distribution(d) for bulk continuous copolymerization of St and MAH with different MAH temperatures (\circ $T = 110\text{ }^{\circ}\text{C}$, \diamond $120\text{ }^{\circ}\text{C}$, \square $125\text{ }^{\circ}\text{C}$; MAH weight fraction in inflow = 7w%, $\tau = 5\text{ h}$; curves as described in Fig. 1)

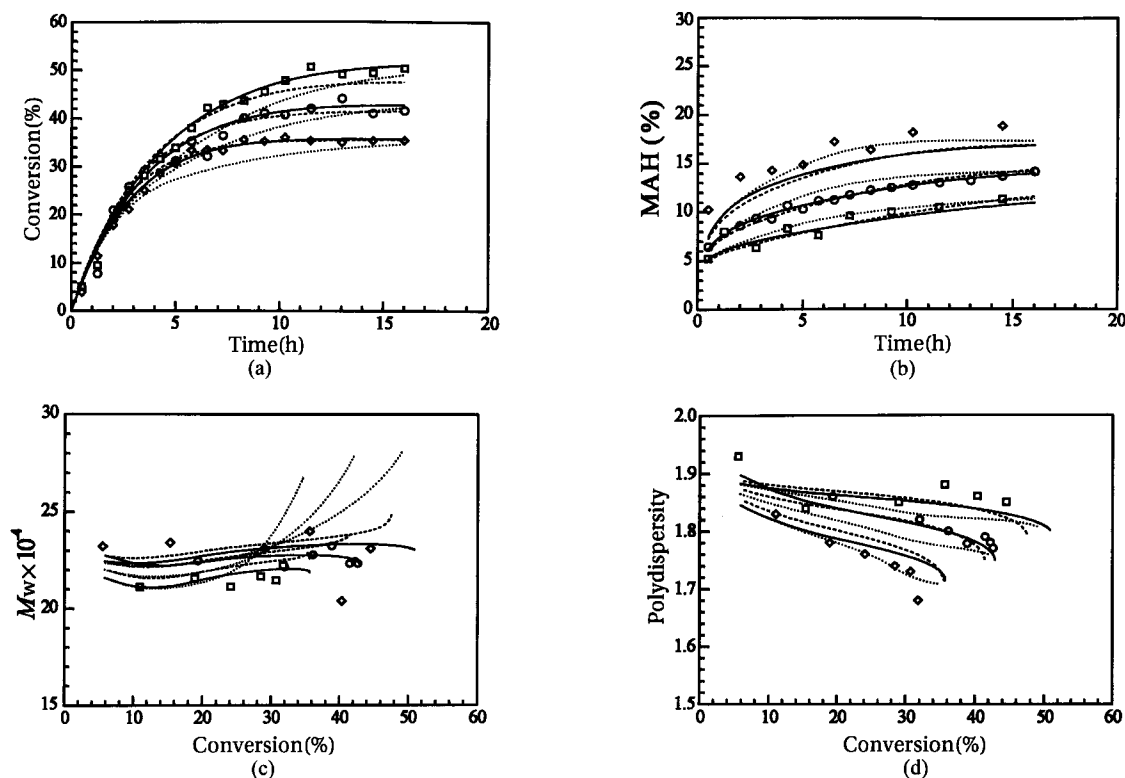


Fig. 5 Conversion(a), copolymer composition(b), molecular weight(c) and its distribution(d) for bulk continuous copolymerization of St and MAH with different residence times (\circ $\tau = 3$ h, \diamond 5 h, \square 7 h; MAH weight fraction in inflow = 7w%, $T = 110$ °C; curves as described in Fig. 1)

The present model and MH model give similar results agreeing very well with experimental data under most operating conditions.

But for all models, the fits between model results and experimental data were poor at very high conversion, which can be reached when the polymerization temperature or the MAH concentration in the reaction mixture is high. In this situation, it is impossible to achieve an instantaneous mixing of the entering low viscous monomers and the existing polymerizing medium in molecular level, and the micro-mixing process may play an important role in altering the outcome of polymerization. The micro-circumstances for variant radicals are different. If a macroscopic variable (bulk viscosity, free volume, and polymer concentration) is used to describe the diffusion phenomena, no good results can be obtained. In this case, a new model with the consideration of micro-mixing is needed.

CONCLUSIONS

A new model was presented to describe the

diffusion controlled polymerization. In this model k_t and k_p were related with the rheological behaviors of the polymerizing mixture. This model was used to simulate the batch bulk thermal polymerization of St and the continuous bulk copolymerization of St and MAH with thermal initiation. The predicted results of the present model and MH, TT models were compared with the experimental data. It was found that only the present model and the MH model can give good results on the monomer-to-polymer conversion, the molecular weight of the polymer and the copolymer compositions. This indicated that rheological data have same predictive power as the free volume to describe the diffusion phenomena in a polymerization system. To calculate the free volume, a large number of parameters are needed, especially for a copolymerization system. The rheological data is easy to get off-line or on-line, and the present model can be conveniently applied to real time control processes. But all three models failed to yield good simulated results at very high conversion.

References

- Achilias, D. S. and Kiparissides, C., 1988. Modeling of diffusion-controlled free-radical polymerizations. *J. Appl. Polym. Sci.* **35**:1303 – 1323.
- Achilias, D.S. and Kiparissides, C., 1992a. Development of a general mathematical framework of modeling diffusion-controlled free-radical polymerization reactions. *Macromolecules*, **25**:3739 – 3750.
- Achilias, D.S. and Kiparissides, C., 1992b. Toward the development of a general framework for modeling molecular weight and compositional changes in free-radical copolymerization reactions. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C32**:183 – 234.
- Bueche, M., 1962. Physical Properties of Polymers. Interscience Publishers, New York.
- Callaghan, P. T. and Pinder, D. N., 1980. Dynamics of entangle polystyrene solutions studied by pulsed field gradient nuclear magnetic resonance. *Macromolecules*, **13**:1085 – 1092.
- Cardenas, J. and O'Driscoll, K. F., 1977. High conversion polymerization. II Influence of chain transfer on the gel effect. III Kinetic behavior of ethyl methacrylate. *J. Polym. Sci., Polym. Chem. Ed.*, **15**: (II)1883 – 1889; (III) 2097 – 2108.
- Chiu, W. Y., Carratt, G. M. and Soong, D. S., 1983. A computer model for the gel effect in free radical polymerization, *Macromolecules*, **16**: 348 – 357.
- de Gennes, P. G., 1971. Reptation of a polymer chain in the presence of fixed obstacles. *J. Chem. Phys.*, **55**: 572 – 579.
- de Gennes, P. G., 1976. Dynamics of entangled polymer solutions. I The rouse model. II Inclusion of hydrodynamic interactions. *Macromolecules*, **9**: (I) 587 – 593; (II) 594 – 598.
- de Gennes, P. G., 1979. Brownian motions of flexible polymer chains, *Nature (London)*, **282**: 367 – 370.
- Duerkon, J. H., Hamielec, A. E., and Hogins, J. W., 1967. Polymer reactors and molecular weight distribution: Part I Free radical polymerization in continuous stirred-tank reactors. *A. I. Ch. E. J.*, **13**: 1081 – 1086.
- Ferry, J. D., 1970. Viscoelastic Properties of Polymer. Wiley-Interscience, New York,
- Fujita, H., 1961. Diffusion in polymer-diluent systems. *Advance in Polym. Sci.*, **3**:1 – 47.
- Fujita, H., 1991. Notes on free volume theories. *J. Polym.*, **23**: 1499 – 1506.
- Hervet, H., Leger, L. and Rondelez, F., 1979. Self-diffusion in polymer solution: A test for scaling and reptation. *Phys. Rev. Lett.*, **42**: 1681 – 1684.
- Hui, A. W. T. and Hamielec, A. E., 1972. Thermal polymerization of styrene at high conversion and temperatures. An experimental study. *J. Appl. Polym. Sci.*, **16**:749 – 769.
- Husain, A. and Hamielec, A. E., 1978. Thermal polymerization of styrene. *J. Appl. Polym. Sci.*, **22**: 1207 – 1223.
- Ito, K., 1980. Evaluation of molecular weight in terms of the gel effect in radical polymerization. *J. Polym.*, **8**: 499 – 506.
- Ito, K., 1981. Estimation of termination rate by the free volume theory in radical polymerization. *J. Polym.*, **13**:727 – 731.
- Jones, C. E. Roland and Reynolds, G. E. J., 1969. Pyrolysis/gas chromatography applied to problem of sequence analysis and microstructure in copolymers. *Brit. Polym. J.*, **1**: 197 – 207.
- Klein, J., 1978. Evidence for reptation in an entangled polymer melt. *Nature (London)*, **271**:143 – 146.
- Marten, F. L. and Hamielec, A. E., 1979. High conversion diffusion-controlled polymerization. *ACS Sym. Ser.*, **104**: 43 – 70.
- Marten, F. L. and Hamielec, A. E., 1982. High-conversion diffusion controlled polymerization of styrene, *J Appl. Polym. Sci.*, **27**: 489 – 505.
- Mendelson, P. A., 1979. A method for viscosity measurements of concentrated polymer solutions in volatile solvents at elevated temperature. *J. Rheology*, **23**: 545 – 556.
- O'Neil, G. A. and Torkelson, J. M., 1997. Recent advances in the understanding of the gel effect in free-radical polymerization. *Trends in Polym. Sci.*, **5**: 349 – 355.
- Sharmal, D. K. and Soong, D. S., 1988. High-conversion diffusion-controlled copolymerization kinetics. *Macromolecules*, **21**: 700 – 710.
- Soh, S. K. and Sunderg, D. C., 1982. Diffusion-controlled vinyl polymerization. I The gel effect. II Limitations on the gel effect. III Free volume parameters and diffusion-controlled. IV Comparison of theory and experiment. *J. Polym. Sci. Polym. Chem. Ed.*, **20**: (I) 1299 – 1314; (II)1315 – 1330; (III)1331 – 1334; (IV)1345 – 1371.
- Tulig, J. T. and Tirrell, M., 1981. Toward a molecular theory of the trommsdorff effect. *Macromolecules*. **14**:1501 – 1511.
- Turner, D. T., 1977. Autoacceleration of free-radical polymerization. I The critical concentration. *Macromolecules*, **10**: 221 – 226.
- Vivaldo-Lima, E., Hamielec, A. E. and Wood, P. E., 1994. Auto-acceleration effect in free radical polymerization. A comparison of the CCS and MAH models. *Polymer Reaction Engineering*, **2**: 17 – 85.
- Vrentas, J. S. and Duda, 1993. J. L., Comparison of free-volume theories. *J. Polym.* **25**: 99 – 101.
- Vrentas, J. S. and Duda, J. L., 1977. Diffusion in polymer-solvent systems. I Reexamination of the free-volume theory. II A predictive theory for the dependence of diffusion coefficients on temperature, concentration, and molecular weight. *J. Polym. Sci., Polym. Chem. Ed.*, **15**:(I) 403 – 416; (II) 417 – 439.
- Yao, Z., Li, B. G., Cao, K. and Pan, Z. R., 1998. Semi-continuous thermal bulk copolymerization of styrene and maleic anhydride-experiments and reactor model. *J. Appl. Polym. Sci.*, **67**: 1905 – 1912.
- Yao, Z., Li, B. G., Wang, W. J. and Pan, Z. R., 1999. Continuous thermal bulk copolymerization of styrene and maleic anhydride. *J. Appl. Polym. Sci.*, **73**:615 – 622.